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ENERGY TRANSFER REACTIONS OF ATMOSPHERIC INTEREST

by

Tom G. Slanger and Graham Black

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Three main areas have been investigated during the term of this contract:

(1) The kinetics of the sources and sinks of $O(^1S)$ in the lower thermosphere have been studied. Measurements have been made of the temperature-dependent rate of the reaction $O(^1S) + O(^3P) \rightarrow 2O$. The production of $O(^1S)$ in an oxygen atom system has been investigated, and comparisons have been made between the so-called Barth mechanism, in which $O(^1S)$ is produced from ground state atoms in

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a two-step process, and the one-step Chapman mechanism. The temperature dependence of this $O(^1S)$ source term has been obtained. On the basis of atmospheric observations, the conclusion is drawn that a better correlation exists between measured oxygen atom concentration profiles and the laboratory data if the source of $O(^1S)$ in the nightglow is the Barth, rather than the Chapman, mechanism.

(2) A determination of quenching rate coefficients for the $NO(B^2\Pi)$ state has been made, using a variety of collision partners. This state, the source of the NO $\beta$-band system, is important in combustion processes.

(3) The first measurements of the product channels in $O(^1S)$ reactions have been carried out, using the five collision partners $N_2O$, $H_2O$, $CO_2$, $O_2$, and NO. All the reactions give high yields of physical quenching, with only $H_2O$ having a significant chemical reaction pathway. Several of these reactions are of practical importance, and the behavior of a system having two alternatives for a physical quenching step $[O(^3P)$ or $O(^1D)]$ is also interesting from a theoretical standpoint.

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## CONTENTS

## ABSTRACT

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## INTRODUCTION

The history of attempts to use the earth's nightglow, particularly the $O(^1S) \to O(^1D)$ emission at 5577 Å, as a monitor for the ground state oxygen atom concentration, stretches back almost half a century to the work of Sidney Chapman.[1] Ever since Chapman proposed that the energy source of the 4.2 eV $O(^1S)$ state is the recombination energy of two oxygen atoms, attempts have been made to obtain the necessary rate coefficients that would convert the observed nightglow intensity into an $O(^3P)$ concentration. The day of success has not yet arrived, but we feel that during the last three years we have made considerable progress in approaching the ultimate answers.

The most needed parameters have been the temperature dependences of the reactions that produce and destroy $O(^1S)$ in the lower thermosphere. It has been known for some time that the principal loss mechanism for $O(^1S)$ is quenching by $O(^3P)$, for which only a $300^\circ$K rate existed in the literature.[2] We were able to measure the rate coefficient between $200^\circ$K and $365^\circ$K, obtaining reasonable agreement with the earlier value. An interesting point is that, although the $O(^1S)-O(^3P)$ system has been considered amenable to calculation, the calculated rate coefficient is three orders of magnitude smaller than the experimental value.[3]

The $O(^1S)$ source term in a laboratory oxygen atom afterglow has been kinetically investigated only once before,[4] because it is difficult, as in any discharge system, to be certain about the identity of all the energy carriers. More information was available on $O(^1S)$ kinetics during the current investigation than during the earlier work, so that it was possible to generate a more self-consistent picture of the system. The measured rate coefficient for $O(^1S)$ production was considerably larger than that previously obtained, and the reaction was found to have a positive activation energy.

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Because there are now a variety of ways of measuring atmospheric $O(^3P)$, the new rate coefficients can be tested by applying them to an $O(^3P)$ profile, calculating the resultant $O(^1S)$ intensity, and seeing if it is realistic. In so doing, it became apparent that the correlation was incompatible with the single-step Chapman mechanism, $3\ O(^3P) \rightarrow O(^1S) + O_2$, but gave a good fit to the Barth mechanism, $2\ O(^3P) + M \rightarrow O_2^*$, $O_2^* + O(^3P) \rightarrow O(^1S) + O_2$, if reasonable assumptions were made as to the kinetic parameters of the intermediate $O_2^*$.

The problem is not yet solved: the identity and reactivity of $O_2^*$ are yet to be determined, a task which we anticipate carrying out in the near future.

The fate of $O(^1S)$ has not been determined in any of the kinetic investigations carried out on $O(^1S)$ in the last several years, it being far simpler to observe the disappearance of 5577 Å radiation than to monitor the appearance of a product. With the precise $O(^1S)$ quantum yield measurements obtained recently in this laboratory,[5] we have been able to decide, for a variety of $O(^1S)$ deactivation reactions, whether the process is physical or chemical quenching and, if physical, whether the $O(^1S)$ is quenched to $O(^1D)$ or $O(^3P)$. No single technique was adequate for these investigations. In most cases, it was possible to get the information from the behavior of the $O(^3P)$ production rate, given the knowledge we now have of all the pertinent $O(^1S)$ and $O(^1D)$ kinetics. For the study of $O_2$, the product channels were obtained by analysis of $O_2(b^1\Sigma_g^+)$ production data; for $CO_2$, continuous monitoring of CO generation led to the required information on $O(^1S)$. This work is a classic example of how one can build on what has gone before, because without the availability of the kinetic data and information on quantum yields, the work would not have been possible.

The studies of the $NO(B^2\Pi)$ quenching rate coefficients were carried out to fill in a significant gap in our knowledge of this important electronic state. Only a few kinetic determinations have been made for the $^2\Pi$ state, even though it is a significant component in many afterglow systems as well as in some combustion processes.

## Unpublished Work

Abstracts of published papers appear in the following subsection, so these papers will not be further described. The major work that is still to be submitted for publication (to the Journal of Chemical Physics) is an extensive study of the product channels for quenching the $O(^1S)$ atom by several diatomic and triatomic collision partners. A variety of techniques were employed to carry out these measurements, and the experience gained over the last several years in the handling of various atmospheric metastable species was extensively utilized. The following paragraphs briefly describe the technique used for each of the five quenching gases; a table of the results obtained follows the descriptions. We were able to distinguish three channels--physical quenching, to give either $O(^1D)$ or $O(^3P)$, and chemical reaction. Except in the case of $N_2O$, the results are unambiguous.

(1)  $\underline{N_2O}$

The total $O(^3P)$ yield was obtained by comparison of the $O(^3P)$ production rate during 1304 Å photolysis with that from $O_2$, in the presence of $N_2$. Thus, any $O(^1D)$ was quenched to $O(^3P)$. Because the total oxygen atom quantum yield from $O_2$ is certainly 2.0, the yield from $N_2O$ was obtained.

Carrying out the same experiment in helium permitted any $O(^1D)$ produced in the $N_2O$ system to react with $N_2O$, preventing it from producing $O(^3P)$. In $O_2$, the $O(^1D)$ was quenched to $O(^3P)$. Any change in $O(^3P)$ quantum yield from the experiment in $N_2$ then established the amount of $O(^1D)$ made from $O(^1S) + N_2O$.

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(2)  $\underline{CO_2}$

It was first determined if the reaction $O(^1S) + CO_2 \rightarrow O_2 + CO$ takes place. This was done by photolytically generating $O(^1S)$ from $CO_2$ at 1048-1067 Å and observing the CO produced, using resonance fluorescence at 1500-1600 Å. CO is made in the initial photodissociation, and if the above reaction takes place, the CO yield could be sharply decreased by addition of an $O(^1S)$ quencher. Both NO and $H_2O$ were used for this purpose.

The yield of $O(^3P)$ from the reaction $O(^1S) + CO_2 \rightarrow O(^3P) + CO_2$ was determined by observing the change in the $O(^3P)$ production rate when $CO_2$ was added during the photolysis of $N_2O$ at 1304 Å in the presence of $H_2$. There was sufficient $CO_2$ to quench most of the $O(^1S)$, and any resultant $O(^1D)$ was removed by $H_2$. Thus, the $O(^3P)$ found after $CO_2$ addition was only that resulting from quenching of $O(^1S)$ to $O(^3P)$ by $CO_2$. The fraction that was quenched to $O(^1D)$ was then obtained by difference.

(3)  $\underline{H_2O}$

Knowing the $O(^3P)$ yield from $O(^1S)$ quenching by $N_2O$, the products of the reaction $O(^1S) + H_2O$ were found by adding sufficient $H_2O$ in the presence of $N_2$ to quench all the $O(^1S)$. The resulting change in the $O(^3P)$ production rate established the total oxygen atoms produced and, by difference, the fraction of $O(^1S)$ reacting chemically with $H_2O$. Carrying out the same experiment in helium gave, by difference, the fraction of $O(^1S)$ quenched to $O(^1D)$.

(4)  $\underline{O_2}$

The $O(^1D)$ yield from $O(^1S) + O_2 \rightarrow O(^1D) + O_2$ was determined by monitoring the $O_2(b^1\Sigma_g^+) \rightarrow O_2(X^3\Sigma_g^-)$ radiation at 7618 Å that follows the reaction $O(^1D) + O_2 \rightarrow O_2(b^1\Sigma_g^+) + O(^3P)$. As $N_2O$

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is added to an $O_2$-He system during 1304 Å photolysis, under conditions where all $O(^1S)$ is quenched by $O_2$, the increasing signal from $O_2(b^1\Sigma_g^+)$ is a measure of the $O(^1D)$ being produced, from which the yield is readily obtainable.

For the above analysis, it is necessary to prove that $O_2(b^1\Sigma_g^+)$ does not result directly from the quenching of $O(^1S)$ by $O_2$, i.e., $O(^1S) + O_2 \rightarrow O_2(b^1\Sigma_g^+) + O(^1D \text{ or } ^3P)$. This was done by first measuring the competitive quenching of $O(^1D)$ by $N_2$ and $O_2$, using the 7618 Å intensity as an $O(^1D)$ monitor. Then, $N_2O$ was again added as a competitive quencher. Because $N_2$ is inefficient at quenching $O(^1S)$, the $O_2(b^1\Sigma_g^+)$ quenching behavior will change drastically if the $O_2(b^1\Sigma_g^+)$ source is $O(^1S)$ instead of $O(^1D)$.

(5)  <u>NO</u>

The $O(^3P)$ yield from $O(^1S) + NO \rightarrow O(^3P) + NO$ [indistinguishable from $O(^1S) + NO \rightarrow N(^4S) + O_2$, $N(^4S) + NO \rightarrow O(^3P) + N_2$] was determined by observing the behavior of the $O(^3P)$ production rate as NO was added to an $N_2O$-He system during 1304 Å photolysis. Because a very small amount of NO quenches all the $O(^1S)$, an abrupt change in the $O(^3P)$ yield can occur. As more NO is added, $N_2O$ quenching of any $O(^1D)$ produced is replaced by NO quenching, so that a rising $O(^3P)$ production rate can be expected.

The $O(^1D)$ yield can be obtained from the above procedure, but a more accurate method is to carry out competitive quenching between an $N_2O$-NO mixture [under conditions where all $O(^1S)$ is quenched by NO] and added $H_2$, which quenches $O(^1D)$ but not $O(^1S)$.

The results shown in Table 1 give information relating to a variety of chemical systems. The $O_2$ result is relevant to $O(^1S)$ quenching in the lower thermosphere and shows that one third of the interactions lead to $O(^1D)$,

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Table 1

PRODUCT CHANNELS IN $O(^1S)$ DEACTIVATION

| | Product Channel (fraction) | | |
| --- | --- | --- | --- |
| Collision Partner | $O(^1D)$ | $O(^3P)$ | Reaction |
| $N_2O^\dagger$ | $0.33 \pm 0.07$ | $0.67 \pm 0.07$ | $0 \pm 0.05$ |
| $CO_2$ | $0.63 \pm 0.05$ | $0.37 \pm 0.05$ | $0 \pm 0.03$ |
| $H_2O$ | $0.30 \pm 0.06$ | $0.09 \pm 0.06$ | $0.61 \pm 0.06$ |
| $O_2$ | $0.31 \pm 0.07$ | $0.69 \pm 0.07$ | --- |
| NO | $0.64 \pm 0.06$ | $0.36 \pm 0.06$ | --- |

---

$\dagger$It is uncertain whether the $O(^3P)$ arises only from quenching $[O(^1S) + N_2O \rightarrow O(^3P) + N_2O]$ or from collisional dissociation $[O(^1S) + N_2O \rightarrow 2\ O(^3P) + N_2]$. If the latter, then as much as 33% of the interaction might proceed through a reactive channel.

which is then available for subsequent reactions. The NO data may be of some importance in aurorae and indicate, among other things, that the reaction $O(^1S) + NO \rightarrow N(^2D) + O_2$, which has been proposed as an $N(^2D)$ source,[6] is not important. The $CO_2$ results show the quenching pathways that can govern $O(^1S)$ behavior in the atmospheres of Mars and Venus. The $N_2O$ results are extremely important for energy storage systems (for laser applications), where it is necessary to know the chemical makeup of a photodissociating system. For instance, NO quenches $O(^1S)$ far faster than do other fragments of an $N_2O$ system. If $O(^1S) + N_2O$ were to make NO exclusively, the subsequent $O(^1S)$ loss rate would be much higher than if other product channels were involved. Unfortunately, we are unable to specify the NO yield completely, since an ambiguity in the $O(^3P)$ source exists (see Table 1). However, adiabatic correlation arguments suggest[7] that a chemical channel, if it exists, would produce $N_2 + O_2$, not 2 NO.

It is not yet possible to make adequate theoretical predictions of the expected behavior of the four-atom systems. For the case of $O(^1S) + NO$, no adiabatic correlations exist between these states and states of $N + O_2$. Therefore, only $O(^1D)$ and $O(^3P)$ are expected as products, as observed.

For the $O(^1S) + O_2$ system, where there is no reactive pathway, it would be interesting to try to correlate what is known about $O_3$ potential energy curves with the observed 31:69 split for $O(^1D):O(^3P)$. Even this system is probably too complicated for an adequate a priori treatment.

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Publications

(1)  $O(^1S)$ Quenching by $O(^3P)$
     Tom G. Slanger and Graham Black
     J. Chem. Phys. <u>64</u>, 3763 (1976)

     The quenching of $O(^1S)$ by $O(^3P)$ was measured as a function of
     temperature, between $200^\circ K$ and $365^\circ K$. The resulting Arrhenius
     expression is $k = 5.0 \times 10^{-11} \exp(-610/RT)$ $cm^3$ $molecule^{-1}$ $sec^{-1}$.
     The possible effect of $O_3$ on the measurements was considered, and it
     is concluded that $O_3$ does not contribute to the observed quenching.
     A sizable discrepancy now exists for this reaction between experiment
     and the most recent theoretical calculations.

(2)  $O(^1S)$ Production from Oxygen Atom Recombination
     Tom G. Slanger and Graham Black
     J. Chem. Phys. <u>64</u>, 3767 (1976)

     An overall rate coefficient of $1.4 \times 10^{-30} \exp(-1300/RT)$ $cm^6$
     $molecule^{-2}$ $sec^{-1}$ was determined for oxygen atom recombination leading
     to production of $O(^1S)$. This rate coefficient refers either to the
     recombination of three oxygen atoms (the Chapman mechanism) or to
     the more conventional recombination of two oxygen atoms with a third
     body, followed by energy transfer from an activated $O_2$ molecule to a
     third $O(^3P)$ atom (the Barth mechanism). Measurements were made between
     $200^\circ K$ and $300^\circ K$, representative of the thermospheric region in which
     the green airglow [the 5577 Å $O(^1S) \rightarrow O(^1D)$ transition] is observed.

(3)  Collisional Quenching of $NO(B^2\Pi_r)_{v'=0}$ Produced by the Reaction of
     $N(^2D)$ with $N_2O$
     G. Black, R. L. Sharpless, and T. G. Slanger
     Journal of Photochemistry <u>5</u>, 435 (1976)

     The reaction of $N(^2D)$ with $N_2O$ has been used as a source of
     $NO(B^2\Pi_r)_{v'=0}$. The effects of added gases on its emission have been
     used to determine quenching rate coefficients (using a radiative
     lifetime of $3 \times 10^{-6}$ s). These coefficients have been compared with
     rate coefficients for quenching the isoenergetic species
     $NO(A^2\Sigma^+)_{v'=0,1}$. The collision partners were He, Ar, $N_2$, $CO_2$, $H_2$,
     $CH_4$, CO, $N_2O$, NO, $O_2$, and $C_2H_4$. Quenching rate coefficients varied
     from $2.9 \times 10^{-13}$ $cm^3$ $molec^{-1} sec^{-1}$ for He and Ar to $3.2 \times 10^{-10}$ $cm^3$
     $molec^{-1}$ $sec^{-1}$ for $C_2H_4$.

(4)   $O(^1S)$ in the Lower Thermosphere--Chapman vs. Barth
      Tom G. Slanger and Graham Black
      Planetary and Space Sciences, <u>25</u>, 79 (1977)

**New data on the production and quenching** of $O(^1S)$ **in the lower
thermosphere have been combined** with current altitude profiles of
5577 $\overset{o}{A}$ intensities and $O(^3P)$ concentrations to show that a persuasive
case can be made for the idea that $O(^1S)$ is generated by the sequence
of steps $O(^3P) + O(^3P) + M \rightarrow O_2^* + M$, $O_2^* + O(^3P) \rightarrow O_2 + O(^1S)$ (the
Barth mechanism), rather than by the reaction $O(^3P) + O(^3P) + O(^3P) \rightarrow$
$O_2 + O(^1S)$ (the Chapman mechanism).  The Chapman reaction is not
entirely excluded, but it now must be considered hypothetical, since
the laboratory data correlate with the atmospheric observations only
through a mechanism involving an intermediate $O_2^*$.  Further work is
needed to establish the identity of this intermediate, which is most
probably the $O_2(A^3\Sigma_u^+)$ state, and to obtain the necessary kinetic
data for a complete description of the system.

(5)   $O(^1S)$ Interactions--The Products
      Tom G. Slanger and Graham Black
      To be published in J. Chem. Phys.

The first measurements are reported of the reaction pathways for
the interaction between oxygen atoms in the 4.19 eV $^1S$ state, and
four molecules, $N_2O$, $CO_2$, $H_2O$, and $NO$.  Distinction is made between
three possible paths--quenching to $O(^1D)$, quenching to $O(^3P)$, and
chemical reaction.  With $N_2O$, the most reasonable interpretation
of the data indicates that there is no reaction, in sharp contrast
with the interaction between $O(^1D)$ and $N_2O$, which proceeds entirely
by reaction.  Similarly, there is no reaction with $CO_2$.  With $H_2O$,
the reactive pathway is the dominant one, although electronic
quenching is not negligible.  With $NO$, $O(^1D)$ is the preferred
product.

## MEETING PRESENTATIONS

"Temperature Dependent Studies of the Reactions $O(^3P) + O(^3P) + O(^3P) \rightarrow O(^1S) + O_2$ and $O(^1S) + O(^3P) \rightarrow 2 O(^1D$ or $^3P)$," paper presented at American Geophysical Union Fall Meeting, San Francisco, Ca., December 8-12, 1975.

"The $O(^1S)$ Airglow--New Laboratory Results," paper presented at 12th Informal Conference on Photochemistry, NBS, Gaithersburg, Md., June 28-July 1, 1976.

"Quenching of $NO(B^2\Pi_r)_{v=0}$ Produced by the Reaction of $N(^2D)$ with $N_2O$," paper presented at 12th Informal Conference on Photochemistry, NBS, Gaithersburg, Md., June 28-July 1, 1976.

## SCIENTIFIC CONTRIBUTORS

Contributors to the research performed under this contract were:

> Tom G. Slanger
> Graham Black
> Robert L. Sharpless

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